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SO YOU WANT TO BUILD A CHLOR-ALKALI PLANT?*

by

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INTRODUCTION

In the world chemical industry, chlor-alkali production occupies a place which was once held by sulphuric acid, its production indicating the development of the industry in general. It involves production of two important chemicals (besides hydrogen), namely chlorine and caustic soda. Chlorine finds application directly and also in the manufacture of a very large number of organic, inorganic and petrochemicals. Most of these usages require large capital investment in high technology fields. Caustic soda on the other hand, is mainly used in rayon, textiles, pulp and paper and soap industries, many of which have been established well in developing countries.

In the highly industrialized countries - the market economies - chlorine, for long, has been ruling the market, with caustic soda lagging behind. Only during the current recession, particularly due to the drop in demand for polyvinylchloride plastic, caustic soda has started tc have an edge on chlorine. In the developing countries, however, the demand for caustic soda has been always more than the demand for chlorine and many of these countries had to face the problem of disposal of chlorine or make part of their caustic soda requirements through the chemical route. For these reasons, most developing countries need only small sized production units.

Until recently, when there was a break-through in the development of a new process, small size plants were not profitable and did not attract reputed consultants /licensors to transfer the technology. The writer has come across at least two instances where clients in developing countries have been advised wrongly. It is hoped that this booklet will provide guidance in the selection of appropriate technology and size for the chlor-alkali plant.

C - Consultant

E - Entrepreneur

E: I have seen in the past few weeks a number of chlor-alkali plants of large sizes and using radically different methods. I have gathered a general impression that only large-sized plants are economically viable. We, in our country, cannot afford a large size plant, nor is there a market, particularly for chlorine. Imports of relatively small quantities of chlorine are expensive due to transport of containers. How should we go about solving this problem?

C: Your problem is not new. Most countries which had their first plant established during the last two decades had the same problem. Chlorine demand for water treatment and sanitation work is always small. Import of chlorine or sodium hypochlorite solution involves heavy freight charges. Similarly, small demand for hydrochloric acid also involves transport of water along with the active ingredient. The solution has been in the past, installation of a larger plant than demanded by chlorine needs and wasting chlorine. This was feasible and actually practised in the fifties and sixties. Many ingenuous methods were developed to waste the chlorine as such or as hydrochloric acid.

E: But that would create environmental problems.

C: Not always. Some of the methods developed were indeed inexpensive and even today could be considered as acceptable. The installation of a larger plant, with partial disposal of chlorine as waste, is not applicable today due to the high cost of energy. As you know, in chlor-alkali plants, electricity is used as a raw material and nearly 4,000 units (KWh) are required for 1 ton of caustic soda along with about 0.88 ton chlorine.

E: That would mean installation of a plant large enough to meet our chlorine needs.

C: Yes, and the balance of caustic soda could always be made by the chemical process.

E: What is the most economical size for a plant? I see that even the large plants employ large numbers of electrolytic cells. How is it that there are still economies of size?

C: It is true that the productive capacity of an electrolytic cell is comparatively small. The economies come in the cost of power rectifier and chlorine handling systems. The voltage across one cell is of the order of about 3.5. With too few cells, the total voltage across the rectifier would be low. The total production is a direct function of KW rating of the rectifier. Today's costs as a function of voltage are somewhat as follows:

Total voltage	Cost in US$ per KW
60	120
70	100
100	78
200	52
300	41
400	36

There will be economies in the other plants handling chlorine and caustic soda.

E: In my visit to various plants, I came across different types of electrolytic cells. How do they differ from each other and how many types are there?

C: Basically, there are three different types of cells. These are mercury cathode,diaphragm cells and membrane cells. In each of these cells, sodium chloride in the salt brine gets split up electrically into sodium and chlorine. Chlorine is always released in the gaseous form. Sodium, in the mercury cathode process, forms an amalgam and the amalgam is continuously removed and reacted with water in a denuder. During decomposition of the amalgamwith water, hydrogen is produced. The strength of caustic soda produced in the denuder depends upon the quantity of water used and is usually of 45-48% strength. There are special designs which can produce up to 70% strength. This caustic is of a very high purity. In the diaphragm cell, the sodium released in the iron cathode reacts with water in the brine and produces caustic soda solution. In order to separate the caustic soda solution (and hydrogen gas evolved) from the chlorine gas, there is a diaphragm of asbestos or similar inert material, and hence the name diaphragm cell. The caustic soda solution is mixed with brine and its strength is kept low to keep the side reactions to the minimum. The solution needs further concentration, during which sodium chloride gets separated out. Some sodium chloride remains in solution and forms a part of marketed caustic soda. The diaphragm cell product, for this reason is unsuitable for the manufacture of rayon unless purified further by expensive treatment.

In the membrane process, which has been commercialized since 1973-74, an ion-exchange membrane is used to separate the cathode products from chlorine. The caustic soda produced is practiclaly free from chloride and has a strength of 30% NaOH or more. Fig. 1 gives the flow-sheet of the process.

E: I have understood now the basic characteristics of the three types. Are they all in use still? Tell me something about their applicability to different situations.

C: Historically, the mercury cell was developed and used most commonly in the UK and Europe. USA developed and used mostly the diaphragm cell. Japan was mostly using mercury cells until the mid-seventies and then had gradually to switch over to the diaphragm or other type after minimata poisoning by mercury (through fish which ingested the metal). For very large-scale operations, mercury cathode and diaphragm cells were competitive - the preference for one or ther other depending upon local circumstances and the use for which caustic soda was made. For small size plants, the mercury cathode cell had certain advantages in investment costs. This was particularly so for medium sized plants in the range of 20 - 50 tons per day caustic soda, and India adopted this type of cell for a major part of its production. The membrane cell, although comparatively new on the scene, is making inroads in all possible fields of application: very small captive plants, small and medium sized plants and very large plants.

E: The development of ion-exchange membrane in fields other than chlor-alkali production is not new. How is it that this process did not suggest itself earlier?

C: Yes, in fact, even for the production of chlor-alkali, the ion exchange membrane was developed as early as 1953. The main problem was clogging-up of the membrane with graphite particles from the anode. Development of metallic anodes from titanium coated with precious metal oxides and the development of better membranes (actually for the fuel cells in space research) helped in the development of commercial cells for chlor-alkali.

E: What is the most economical size of a chlor-alkali plant?

C: This is a very difficult question to answer. It varies from country to country and depends on the local conditions. Fortunately, with the development of membrane cells, the answer is simple today.

In some areas in the USA,for example, a 250 metric tons/day plant, even though long in existence (and therefore depreciated), is no more viable. Plants of this size and smaller are closing down. In India, new installations are not considered viable unless they are larger than 50 tons per day. In both these cases the question of internal competition plays the main role in determining the economic size.

For a country like yours,considering the installation of its first chlor-alkali facility, the economic size is even smaller. For captive use of chlorine, there are electrolytic cells of very small size catering for water sterilization, small paper or textile mills and so on. This does not cover what you have in mind, but a 10 to 20 tons per day capacity plant could be considered viable in most cases.

E: The consumer has often a large voice and argues for a low price for development of consumer industries.

C: In the long run for healthy development of soap, textiles, paper and pulp and other industries, stability in prices and regular supplies (independent of availability of foreign exchange) are more important than low prices for a short duration. International prices tend to fluctuate considerably depending upon the balance of supplies between caustic soda and chlorine. For example, the prices of caustic soda have firmed up considerably during the past 2 years due to lower demand of chlorine. Then again, for a basic chemical industry such as chlor-alkali manufacture, a long-term view of general industrial development of the country dictates its early establishment, even with a lower cost-benefit ratio.

E: For the small-sized plant we are talking about, which type of cell do you recommend?

C: In the past, both mercury and diaphragm types of cells have been used in small sized plants. With the development of membrane cells, the diaphragm cell has lost whatever advantage it had. In the case of mercury cells, the environmental problem has to be examined. In modern installations the losses of mercury have been reduced to a small fraction of what was considered unavoidable only a decade or two ago. But these techniques of recovery or preventing mercury losses can be installed only in large plants and are quite expensive in the first costs. Then we should not forget about loss of mercury by theft, which sometimes means a difference between profit and loss. For a small sized plant from 5 - to 50 tons per day, you can almost generalize that the membrane cell is the best choice.

E: Are there different designs for the membrane cells? Who are the usual suppliers of these cells?

E: As in the case of the two older types of cells, there is a number of different designs available. Most of the suppliers of the two older types of cells have taken up the supplies of the membrane cells. The suppliers of ion-exchange membrane and titanium-substrate anodes are limited. These important components are also supplied (even as replacements) by the people who supply the whole plant. The technology of fabrication of titanium substrate anodes has reached a mature stage. For the membrane, there are two different types developed independently by DuPont in the USA and Asahi Glass Co . in Japan, DuPont material goes by the trade name Nafion and the Japanese membrane by Flemion. The membranes lose their activity slowly and need replacement about once in 3 years. The anodes require recoating every 5-7 years.

E: Do you have some idea of the cost of a small - say 5 tons per day - chlor-alkali plant and the requirements of raw materials and utilities?

C: Yes , I can give you the order of magnitude of the investment costs and raw material/utilities requirements, enough for a preliminary examination of the project. These figures get modified to the extent of elements of freight, customs duty etc. A 5 metric tons per day caustic soda plant would cost today (1983) about US$ 3 million erected ready for operation. Raw materials/utilities requirements will be:

	Usage per Year for 1,650 m.tons NaOH
Salt	2,500 tons
Hydrochloric acid	50 tons
Soda ash	60 tons
Miscellaneous	$ 2 per ton NaOH
Anode recoat	$ 10 " " "
Membrane replacement	$ 10 " " "
Electricity(cells)	4.0 million KWh
Electricity (Auxilliary)	0.2 " "
Water make-up	12,000 m^3
Water for rectifier	120,000 m^3

Appendix 1 gives some important features and characteristics of these cells and specifications of products made.

E: We discussed earlier that with the present day problems it is not feasible to waste chlorine to make more caustic soda. Could you tell me briefly about the chemical method of caustic production?

C: The process is simple. You causticize a 10-12% solution of soda ash with a thick (250 gms per litre CaO) milk of lime at about 90^{o} C in a series of agitated reaction tanks and separate the calcium carbonate mud by decantation and counter-current washing. The precipitated carbonate is finally filtered and washed to recover most of the alkali. The caustic soda solution is concentrated in multiple-effect evaporators using steam. (See Fig. 2).

E: Can we recover the carbonate mud as precipitated calcium carbonate - a really high value by-product?

C: I am afraid not. Its physical characteristics are very different. In order to reduce the size of the equipment and reduce the loss of alkali, operating conditions are adjusted to get the heaviest possible precipitate. Then again, lime used for causticization contains enough impurities to render the precipitate useless for any other use except for reburning to produce lime or in the manufacture of cement.

E: Can this plant be integrated with a chlor-alkali plant?

C: If hydroelectric power or other external sources of power are not available, and if it is necessary to generate the power for the chlor-alkali plant at site, the chemical caustic soda plant will permit the installation of a high-efficien y thermal power plant using back-pressure turbines. The ideal integration of the chemical caustic plant is really with a soda ash plant. A solution of soda ash can be obtained more economically by wet calcination of crude sodiumbicarbonate in a solvay process plant. In a natural soda plant, the initial brine obtained by solution mining or sub-soil or lake brine can be used with advantage.

E: Is the technique of evaporation of caustic soda solution different from evaporation of diaphragm cell caustic effluent?

C: Yes. In the chemical caustic formation about 8-10% of soda ash remains unconverted. Higher conversion can be obtained only if the concentration of sodium carbonate is lowered which would mean more steam consumption in the evaporators. The removal of unconverted sodium carbonate is tricky. It is best removed as a triple salt of carbonate, sulphate and chloride of sodium. In order to recover sodium carbonate, these salts are recirculated through the causticization plant. To keep a proper balance of these three salts, particularly the sulphate balance, either the fished salts are purged from the system from time to time or some sodium sulphate is added to the system.

E: Is not the chemical process obsolete?

C: Only in the highly industrialized countries where chlorine demand was ruling the market for all these years. Even in these countries, the recent trend has shown a reversal of the role. The chemical caustic process is in use in a number of developing countries.

E: Here again, could you give me some idea of capital investment and materials and utilities consumption?

C: I have with me investment figures for 1981 for a 25 tons per day plant which I believe will be of use to you. The total battery limit plant costs for such an installation is estimated to cost US$ 5.5 million in a developing country with the major part of the equipment (except tankage in mild steel) imported. If you take about 18-20% higher figures, it will give you the present day cost. The estimate is for a 46-48% NaOH concentration and excludes fusion plant. The requirements of raw materials and

utilities are as follows, again for a facility manufacturing 46-48% caustic soda:

	Quantities per metric ton NaOH
Soda ash	1.4 tons
Limestone (without reburning)	2.9 tons
Steam at 8.5 ATA	3,100 kg
Circulating cooling water	225 m^3
Process water	10 m^3
Power	230 kWh
Fuel oil (for sludge reburning)	225 litre
or coke (for lime burning)	280 kg

E: Of the two processes, electrochemical and chemical, which one makes cheaper caustic soda?

C: That depends mainly upon the cost of power for the electrochemical process at which you can get soda ash for the causticization process. But then, you should appreciate that these processes are not competititve from a national point of view. To the extent that you need chlorine and its products, you have to follow the electrolytic route, even if the cost of production of caustic soda is somewhat higher. Vice versa, even if the electrolytic caustic works out more profitable, you cannot produce more by this process, beyond your chlorine needs. Exports of chlorine or chlorine products are unprofitable from a small sized plant.

E: How do you compute the cost of chlorine and caustic soda in a chlor-alkali plant?

C: Yes , this is an important question. A similar question arises when you generate power and steam at lower pressure in a thermal power plant having a back-pressure turbine. The practice in India when part of the chlorine was wanted, was to take chlorine as a by-product, take credit for sales of chlorine (and chlorine products), and calculate the cost of production of caustic soda. In the USA where caustic soda so far was a subsidiary product, the practice is to express the total cost as cost per ton ECU or electrochemical unit i.e. 1 ton of chlorine plus about 1.11 tons NaOH + 28.6 kg hydrogen. In the concept of cost per ECU, there is no separation of cost elements for different products. Whichever method is used, it will be arbritary and any method which does not have some flexibility may prove to be inconvenient whenever there are shifts in demands for caustic soda and chlorine.

E: I do not understand why we should go for a chlor-alkali plant if we can make caustic soda cheaper through the chemical way.

E: As I said above, one reason is for meeting the legitimate needs for chlorine and chlorine products. The major consideration, however, is that the development of the chlor-alkali industry leads to a healthy development of the chemical industry in general on a broad spectrum, ultimately leading to the manufacture of insecticides, pesticides, plastics, synthetic fibres and a whole range of petrochemicals.

E: Thank you for this very interesting discussion. Only one more question remains. With the preliminary data given by you, it will be possible for our people to prepare a preliminary report for discussion with government officials. Such a report, naturally, cannot be presented to a financial institution for any loans. How do we go about preparing a detailed feasibility report acceptable to these financing institutions?

C: Well, you can approach the UNDP office in your country and suggest that the preparation of such a feasibility study be undertaken. They will then include it in the Country Programme and UNIDO will find an expert to prepare such a report which can form the basis of the establishment of such an industry in your country.

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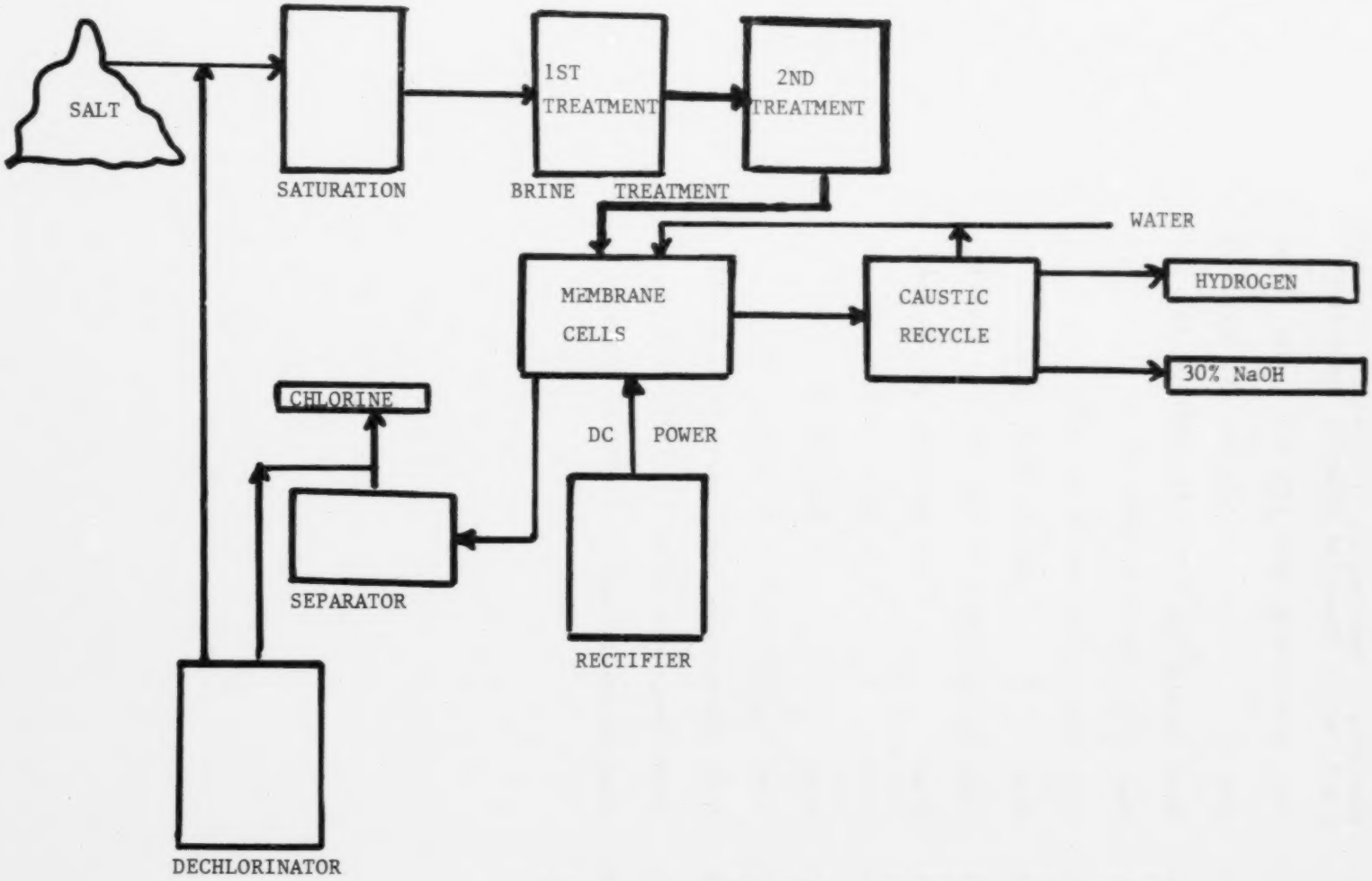

FIG 1 FLOW SHEET MEMBRANE CELL PLANT

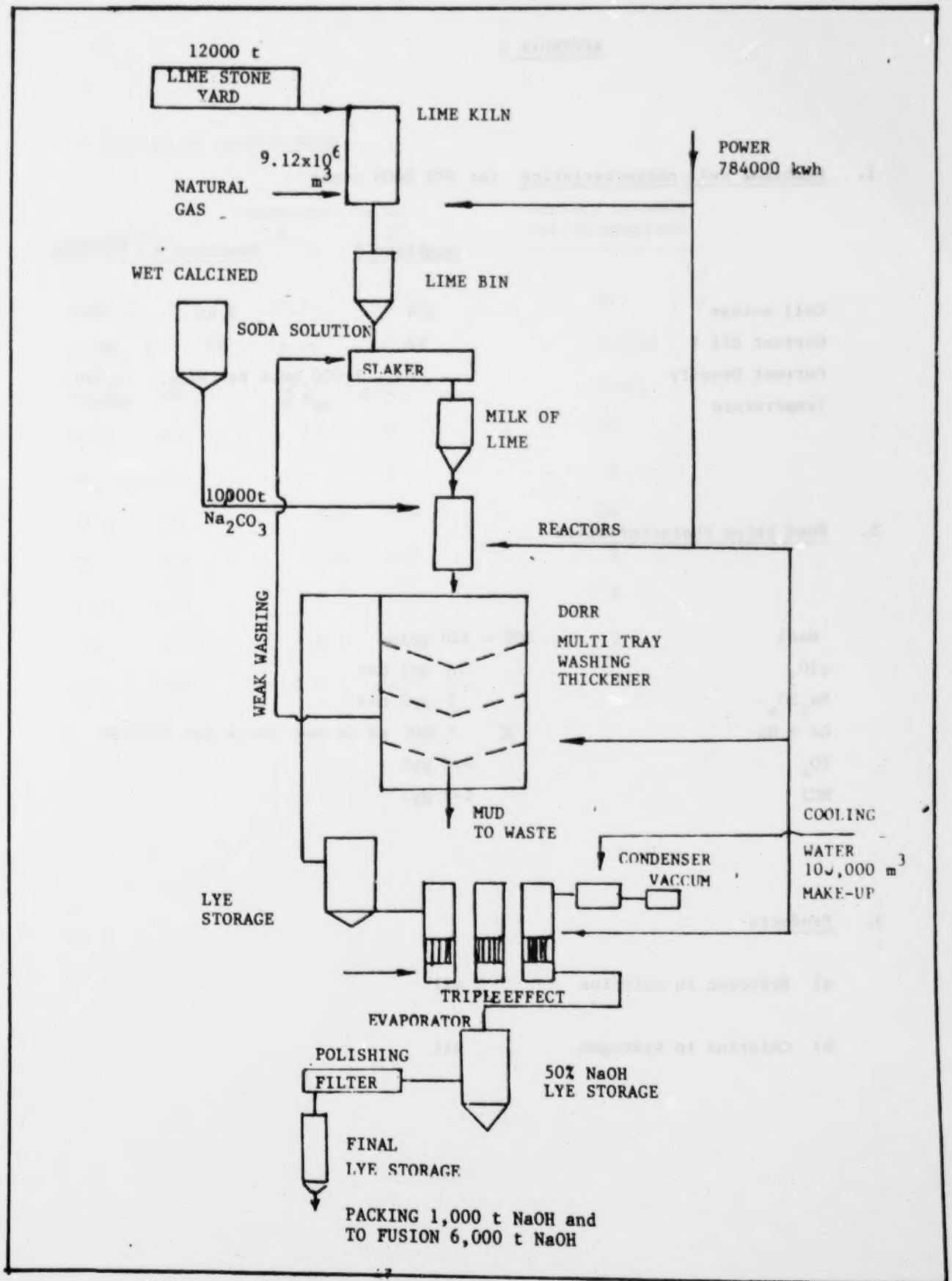

FIG 2 CHEMICAL CAUSTIC SODA 7000 tons/year

APPENDIX 1

1. Membrane cell characteristics (at 30% NaOH cone)

	Membrane A	Membrane B	DE NORA
Cell votage	3.4	3.65	3.2
Current Eff %	92	95	95
Current Density		2,000 amps per sq.m.	3,000 amps
Temperature		90^{o} C	

2. Feed brine characteristics

Nacl	300 - 320 gpl
clO_3	10 gpl max
Na_2SO_4	5 gpl max
Ca + Mg	< 5 ppb as Ca max parts per billion
PO_4	0.2 gpl
HCl	1-2 gpl

3. Products

a) Hydrogen in chlorine nil

b) Chlorine in hydrogen nil

c) Quality of caustic soda

Components	Membrane Cells I	II	Mercury cathode cell(comparison)
NaOH %	35.5	40.12	50
Na_2CO_3 %	0.03	0.01	0.033
$NaClO_3$ ppm	< 10	< 10	Trace
NaCl ppm	15	9	20
Na_2SO_4 ppm	-	1	2
SiO_2 ppm	1.3	1.8	20
Fe ppm	1.4	1.4	3
Al_2O_3 ppm	0.3	0.3	4
CaO ppm	0.1	0.12	3
MgO ppm	< 0.1	< 0.1	3